NAS Technical Report; NAS-07-006
August 2007

Anharmonic vibrational spectroscopy calculations with electronic structure potentials: comparison of MP2 and DFT for organic molecules

Galina M. Chaban*

NASA Ames Research Center, Mail Stop T27B-1, Moffett Field, CA 94035-1000, USA

R. Benny Gerber

Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel; and

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

Abstract

Density Functional Theory (DFT) technique is the most commonly used approach when it comes to computation of vibrational spectra of molecular species. In this study we compare anharmonic spectra of several organic molecules such as allene, propyne, glycine, and imidazole, computed from ab initio MP2 potentials and DFT potentials based on commonly used BLYP and B3LYP functionals. Anharmonic spectra are obtained using the direct Vibrational Self-Consistent Field (VSCF) method and its correlation-corrected extension (CC-VSCF). The results of computations are compared with available experimental data. It is shown that the most accurate vibrational frequencies are obtained with the MP2 method, followed by the DFT/B3LYP method, while DFT/BLYP results are often unsatisfactory.

* E-mail: gchaban@mail.arc.nasa.gov

Keywords: ab initio calculations, density functional calculations, electronic structure, vibrational anharmonicity, vibrational spectroscopy, vibrational self-consistent field.

Introduction

Theoretical computation of vibrational frequencies has become almost "a must" for experimental spectroscopists these days, as it helps to interpret and assign experimental infrared or Raman spectra, especially in difficult and questionable cases. If one takes a look over any recent issue of, for example, Spectrochimica Acta (where new experimental spectra of organic molecules are reported), almost any article contains theoretical computations that help to interpret experimental findings. Another brief look shows that these theoretical data are almost exclusively obtained at the harmonic level using Density Functional Theory (DFT), most often with BLYP and B3LYP functionals. The latter is considered to provide the most accurate vibrational frequencies of organic compounds, provided that the calculated frequencies are scaled (most often, by a uniform scaling factor) to compensate for all possible sources of inaccuracy, both those that are due to inaccuracies of electronic structure methods (such as basis set deficiencies and approximate treatment of electron correlation) and those that are due to the inaccuracies of the treatment of nuclear motions (lack of corrections for anharmonicity).

In this study, we are going to show that the accuracy of vibrational frequencies computed with the most commonly used DFT methods is overrated. When anharmonic corrections are computed explicitly (rather than accounted for by scaling factors), it becomes more evident that the popularity of DFT techniques for this purpose should be partially attributed to a fortuitous cancellation of errors mentioned above. This is

especially true for high frequency vibrations such as X-H stetches (where X is C, N, or O atom). Namely, the errors due to the harmonic approximation that lead to the *overestimation* of vibrational frequencies compensate the errors due to the deficiencies of the DFT electronic structure methods that lead to a similar *underestimation* of vibrational frequencies.

In order to account for anharmonicities explicitely, we use ab initio CC-VSCF method [1], which is one of the several direct ab initio anharmonic vibrational spectroscopy algorithms that has been developed in the recent years [2-6]. The method utilizes potential energy points computed directly from electronic structure programs and accounts for both one-dimensional anharmonic corrections and couplings between vibrational normal modes. The ab initio CC-VSCF technique is based on first principles and does not require fitting of potential energy surfaces, nor does it require any empirical parameters or scaling factors. It works entirely within an electronic structure package and is a very general technique that can be applied to any molecule of reasonable size and to employ potentials computed with any electronic structure method of choice.

In conjunction with the MP2 and CCSD(T) electronic structure methods, the CC-VSCF approach was previously shown to provide reliable anharmonic vibrational data for a variety of molecular and ionic systems, such as water clusters and complexes of negative and positive ions with water [7,8], complexes of inorganic acids with water [9-12], and complexes of organic molecules with water [13-15]. Use of CC-VSCF with DFT potentials was previously tested as well [16,17] for water molecule, water dimer and $Cl^-(H_2O)$. Here we test the performance of some of the most popular DFT functionals for

larger molecules such as allene, propyne, glycine, and imidazole and compare the computed spectra with those obtained with the MP2 potentials.

Methodology

Geometry optimizations, harmonic and anharmonic vibrational spectra calculations were performed at the second order Møller-Plesset perturbation theory (MP2) [18], DFT(BLYP) [19] and DFT(B3LYP) [20] levels of theory. Dunning's triple ζ + polarization (TZP) basis set [21] was used for allene and propyne, while Dunning-Hay double ζ + polarization (DZP) basis set [22] was employed for glycine and imidazole. Anharmonic vibrational frequencies have been obtained using the Vibrational Self-Consistent Field (VSCF) method [23,24] and its Correlation Corrected (CC-VSCF) extension via second-order perturbation theory [25].

The VSCF method [23,24] is based on a separability approximation, where the total vibrational state of the system is represented by a product of one-dimensional wave functions:

$$\Psi = \prod_{j}^{N} \psi_j(Q_j) \qquad (1)$$

(N is the number of vibrational degrees of freedom, Q_j are mass-weighted normal coordinates). The VSCF approximation reduces the problem of solving the N-dimensional vibrational Schrödinger equation to solving N single-mode VSCF equations. The resulting VSCF solutions are further corrected for correlation effects between the vibrational modes using second order perturbation theory (CC-VSCF) [25]. A combined ab initio/CC-VSCF approach has been described in detail previously [1,2]. The method uses a pairwise approximation for the potential [25], where the potential of the system is represented by the

sum of separable (single mode) terms and pair coupling terms, neglecting interactions of triples of normal modes and higher-order interactions:

$$V(Q_1,...,Q_N) = \sum_{j}^{N} V_j^{diag}(Q_j) + \sum_{i}^{N-1}\sum_{j>i}^{N} V_{ij}^{coup}(Q_i,Q_j) \qquad (2)$$

"Diagonal" (single-mode) terms $V_j^{diag}\left(Q_j\right) = V(0,...,Q_j,...,0)$ and the pairwise mode-mode coupling terms $V_{ij}^{coup}\left(Q_i,Q_j\right) = V(0,...,Q_i,...,Q_j,...,0) - V^{diag}(Q_i) - V^{diag}(Q_j)$ are calculated directly from the electronic structure program on 16 point grids along each normal coordinate, and on 16x16 square grids for each pair of normal coordinates. The calculated potentials are then used for numerical solution of the one-dimensional VSCF equations.

All calculations in this study were performed using the electronic structure package GAMESS [26]. No symmetry (C_1 point group) was used in the calculations presented here. The reason for this is that the current VSCF codes are not symmetry adapted. As a consequence, the degenerate vibrational frequencies are often split at the VSCF and CC-VSCF levels due to numerical errors. We note that in principle, there can be cases where the system shows degeneracies at the harmonic level, which are physically lifted when anharmonicity is rigorously included, since the symmetry group associated with the full vibrational Hamiltonian is not always the same as that of the harmonic approximation. However, more typically the degeneracy breaking seen in VSCF calculations is artificial, due to numerical errors in treating the two different transitions. We believe that this is the origin of the degeneracy breaking in the examples presented here. The magnitude of splittings is however within the errors of the CC-VSCF method and much smaller than the inaccuracies in the potentials computed by electronic structure methods.

Results and discussion

Geometrical structures of the four molecules considered in this study are shown in Fig.1. Their equilibrium geometrical parameters computed at all three levels of theory (BLYP, B3LYP, and MP2) are available to interested readers upon request. Here we concentrate our attention on the presentation of the computed vibrational frequencies. Tables 1-4 list both computed (harmonic and anharmonic) and experimental vibrational frequencies for allene, propyne, glycine, and imidazole, respectively. The experimental data for allene and propyne are taken from the NIST database [27], for glycine – from Ar matrix infrared measurements [28], for imidazole – from the gas phase infrared spectra [29]. Absolute deviations of the calculated *anharmonic* frequencies from experimental values are plotted against the experimental frequencies in Figs 2-5.

In the cases of allene and propyne (tables 1 and 2 and figures 2 and 3) it can be seen that the accuracy of computed anharmonic values obtained at all three levels of theory is comparable for a wide region of vibrational frequencies, except for C-H stretching vibrations. The C-H stretches are predicted much more accurately by the MP2 method, with the average errors of 25 and 32 cm^{-1} for allene and propyne, respectively. The corresponding average errors at the B3LYP level are 101 and 87 cm^{-1}; and at the BLYP level – 191 and 173 cm^{-1}. It should be noted that BLYP frequencies are *underestimated* throughout the whole spectrum of both allene and propyne molecules, but this underestimation is most pronounced for the C-H stretches. Similar underestimation can be also observed for glycine and imidazole molecules (Fig. 4 and 5, tables 3 and 4). Here, MP2 and B3LYP methods are of good and comparable accuracy in the low frequency (up to 1500-2000 cm^{-1}) regions, with the average errors on the order of 20-30

cm^{-1}, while BLYP frequencies are systematically underestimated, with the errors noticeably larger (40-60 cm^{-1} on average). In the high frequency regions (corresponding to O-H, N-H, and C-H stretching vibrations), MP2 potentials produce the smallest errors (with the average of 18 cm^{-1} for glycine and 24 cm^{-1} for imidazole), followed by the B3LYP ones (48 and 102 cm^{-1}), and BLYP being the least satisfactory, with very large errors of 150 and 230 cm^{-1}.

It can be concluded that DFT(B3LYP) method (most commonly used in the literature to compute vibrational frequencies of organic molecules) does very well for low frequency vibrations such as bending and torsional modes. However, it *underestimates* higher X-H stretching frequencies (where X=O,N,C) by large amounts (from 50 to 100 cm^{-1}). As to the DFT(BLYP) method, its performance is less satisfactory than that of B3LYP throughout all regions of the spectra, with the worst results produced for the high frequency stretching vibrations (underestimations are on the order of 200 cm^{-1}). It can be seen from the tables that BLYP *harmonic* values for these stretching frequencies (which are also greatly underestimated) are in a closer agreement with experimental values than the anharmonic ones! This fortuitous cancellation of two huge errors (one coming from the lack of anharmonic corrections and the second coming from the underestimation of harmonic frequencies), both on the order of 200 cm^{-1}, is the reason for this method being so popular and widely used by experimental chemists to compute vibrational frequencies of organic molecules. It becomes clear that when anharmonic corrections are properly accounted for, DFT methods give much less satisfactory results (especially, for the high frequency X-H stretching vibrations) than the MP2 approach.

It should be noted that for bending and torsional modes there are cases where

DFT/B3LYP method appears to produce more accurate results than MP2 (see, for example, the errors for glycine, Fig. 4, in the region between 800 and 1800 cm^{-1}). However, the experimental frequencies used for comparison in this case are measured in Ar matrix, where they are somewhat shifted to the red due to interactions of glycine molecule with Ar atoms. For example, the O-H stretching frequency of glycine obtained in He droplets[30], where the matrix effects are much smaller, is 25 cm^{-1} higher than that measured in Ar. This is also consistent with the data for imidazole (Fig. 5), for which gas phase experimental values are available for comparison. Here it is seen that most of the B3LYP frequencies are *below* experimental values even in the low (500-1500 cm^{-1}) frequency region of the spectrum. Comparison of experimental data obtained for imidazole in different environments [31-35] also shows that Ar matrix isolation studies provide lower values of vibrational frequencies than gas phase and He droplet measurements.

Conclusions

We have performed calculations of anharmonic vibrational frequencies of four organic molecules (allene, propyne, glycine, and imidazole) using potentials obtained at three different levels of theory: DFT/BLYP, DFT/B3LYP, and MP2. The deviations of the computed vibrational frequencies from experimental data are obtained and compared. It is found that the most accurate results are provided by MP2 potentials, especially in the regions of high frequency X-H stretching vibrations (X=C, N, O). DFT potentials are found to produce underestimated values for these high frequency vibrations. While use of the B3LYP functional provides accurate data for lower frequency regions of bending and

torsional modes, the use of the BLYP functional leads to very poor results in all regions of spectra. The wide use of DFT methods in the literature for computation of vibrational spectra of organic molecules can partially be attributed to the fortuitous cancellation of two errors of the opposite sign: neglect of anharmonicity that leads to overestimation of vibrational frequencies and deficiency in the DFT treatment of electronic structure that results in their underestimation.

A legitimate question is whether the results reported here could be affected by the limited accuracy of the CC-VSCF, the vibrational algorithm used. It seems to us that this is very unlikely for the following reasons. First, the extensive record of previous applications of CC-VSCF (see, for example, Ref.1) seems to indicate that CC-VSCF errors are sufficiently small to exclude this possibility in most cases. This is especially true for hydrogenic stretching modes, for which the differences between DFT and MP2 predictions are quite large, and well exceed typical CC-VSCF errors for these vibrations. Another (and also very important) reason is the very systematic nature of the results for several different systems. This seems to strengthen the interpretation that the difference between the accuracies of MP2 and DFT variants reflects mostly on the properties of the electronic structure methods.

Acknowledgements

We wish to dedicate this paper to Professor Mark S. Gordon, a teacher of one of us (GMC) and a friend of the second author, in appreciation of everything we have learned from him. This work was in part supported by a grant from the US-Israel Binational Science Foundation (BSF 2004004, to RBG and M. S. Gordon).

References

1. Gerber, R. B.; Chaban, G. M.; Brauer, B.; Miller, Y. (2005) First - Principles Calculations of Anharmonic Vibrational Spectroscopy of Large Molecules. In "*Theory and Applications of Computational Chemistry: The First 40 Years (A Volume of Technical and Historical Perspectives)". EDITED BY: Clifford E. Dykstra, Gernot Frenking, Kwang S. Kim, and Gustavo E. Scuseria*. Elsevier, 165-194.

2. Chaban, G. M.; Jung, J.-O.; Gerber, R. B. (1999) *J. Chem. Phys. 111*, 1823.

3. Yagi, K.; Taketsugu, T.; Hirao K.; Gordon, M. S. (2000) *J. Chem. Phys. 113*, 1005.

4. Irle, S.; Bowman, J. M. (2000) *J. Chem. Phys.*, *113*, 8401.

5. Barone, V. (2004) *Chem. Phys. Lett. 383*, 528.

6. Rauhut, G. (2004) *J. Chem. Phys. 121*, 9313.

7. Chaban, G. M.; Jung, J.-O.; Gerber, R. B. (2000) *J. Phys. Chem. A*, *104*, 2772.

8. Chaban, G. M.; Xantheas, S. S.; Gerber, R. B. (2003) *J. Phys. Chem. A*, *107*, 4952-4956.

9. Chaban, G. M.; Gerber, R. B.; Janda, K. C. (2001) *J. Phys. Chem. A*, *105,* 8323.

10. Chaban, G. M.; Gerber, R. B. (2002) *Spectrochim. Acta A*, *58*, 887.

11. Miller, Y.; Chaban, G. M.; Gerber, R. B. (2005) *Chem. Phys. 313*, 213-224.

12. Miller, Y.; Chaban, G. M.; Gerber, R. B. (2005) *J. Phys. Chem. 109*, 6565-6574.

13. Chaban, G. M.; Gerber, R. B. (2001) *J. Chem. Phys. 115*, 1340-1348.

14. Gerber, R. B.; Chaban, G. M.; Gregurick, S. K.; Brauer, B. (2003) *Biopolymers*, *68*, 370.

15. Chaban, G. M. (2004) *J. Phys. Chem. A*, *108*, 4551-4556.

16. Wright, N. J.; Gerber, R. B. (2000) *J. Chem. Phys. 112*, 2598.

17. Wright, N. J.; Gerber, R. B.; Tozer, D. J. (2000) *Chem. Phys. Lett. 324*, 206.

18. Pople, J. A.; Binkley, J. S.; Seeger, R. (1976) *Int. J. Quantum Chem. 10*, 1.

19. (a) Becke, A. D. (1988) *Phys. Rev. A*, *38*, 3098; (b) Lee, C.; Yang, W.; Parr, R. G. (1988) *Phys. Rev. B*, *37*, 785.

20. (a) Becke, A. D. (1993) *J. Chem. Phys. 98*, 5648; (b) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. (1994) *J. Phys. Chem. 98*, 11623; (c) Hertwig, R. H.; Koch, W. (1997) *Chem. Phys. Lett. 268*, 345.

21. Dunning, T. H. (1971) *J. Chem. Phys. 55*, 716.

22. Dunning, T. H. and Hay, P. J. (1977) Methods of Electronic Structure Theory, edited by H. F. Schaefer, Plenum, NY, Chap. 1, pp. 1–27.

23. Bowman, J. M. (1986) *Acc. Chem. Res. 19*, 202.

24. Ratner, M. A. and Gerber, R. B. (1986) *J. Phys. Chem. 90*, 20.

25. Jung, J.-O. and Gerber, R. B. (1996) *J. Chem. Phys. 105*, 10332.

26. (a) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. (1993) *J. Comp. Chem. 14*, 1347;
(b) http://www.msg.ameslab.gov/GAMESS/GAMESS.html.

27. Shimanouchi, T. (1972) Tables of Molecular Vibrational Frequencies Consolidated Volume I, National Bureau of Standards, 1-160.

28. Stepanian, S. G.; Reva, I. D.; Radchenko, E. D.; Rosado, M. T. S.; Duarte, M. L. T. S.;

Fausto, R.; Adamowicz, L. (1998) *J. Phys. Chem. A*, *102*, 1041.

29. Majoube, M.; Vergoten G. (1992) *J. Mol. Struct. 266*, 345.

30. Huisken F.; Werhahn O.; Ivanov, A. Yu.; Krasnokutski, S. A. (1999) *J. Chem. Phys. 111*, 2978.

31. King, S. T. (1970) *J. Phys. Chem. 74*, 2133.

32. Van Bael, M. K.; Smets, J.; Schoone, K.; Houben, L.; McCarthy, W.; Adamowicz, L.; Nowak, M. J.; Maes G. (1997) *J. Phys. Chem. A*, *101*, 2397.

33. Billes, F.; Endrédi, H.; Jalsovszky, G. (1999) *Journal of Molecular Structure (Theochem) 465*, 157.

34. El-Azhary, A. A. (2003) *Spectrochim. Acta A*, *59*, 2009.

35. Choi, M. Y.; Miller, R. E. *(*2006) *J. Phys. Chem. A, 110,* 9344.

Figure captions

1. Geometrical structure of allene, propyne, glycine, and imidazole molecules.

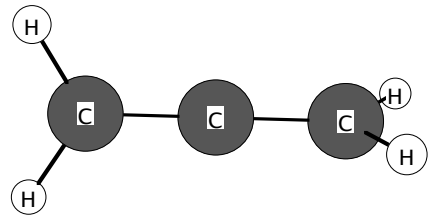
2. Comparison of BLYP, B3LYP, and MP2 methods for allene molecule.

3. Comparison of BLYP, B3LYP, and MP2 methods for propyne molecule.

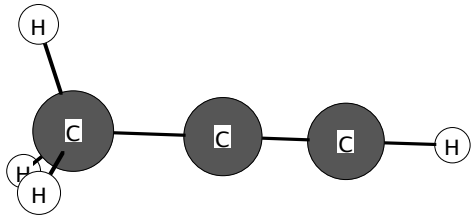
4. Comparison of BLYP, B3LYP, and MP2 methods for glycine molecule.

5. Comparison of BLYP, B3LYP, and MP2 methods for imidazole molecule.

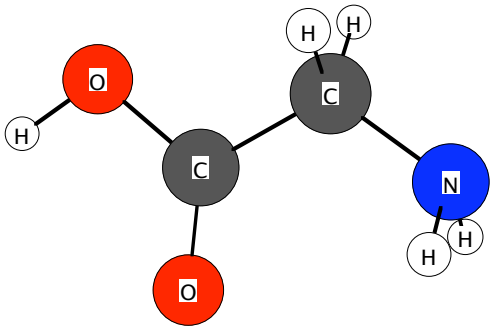
allene



propyne



glycine



imidazole

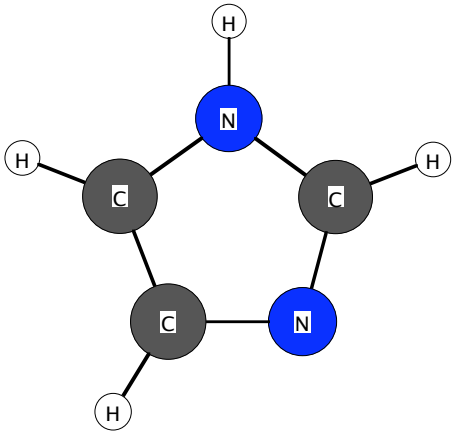


Fig. 1

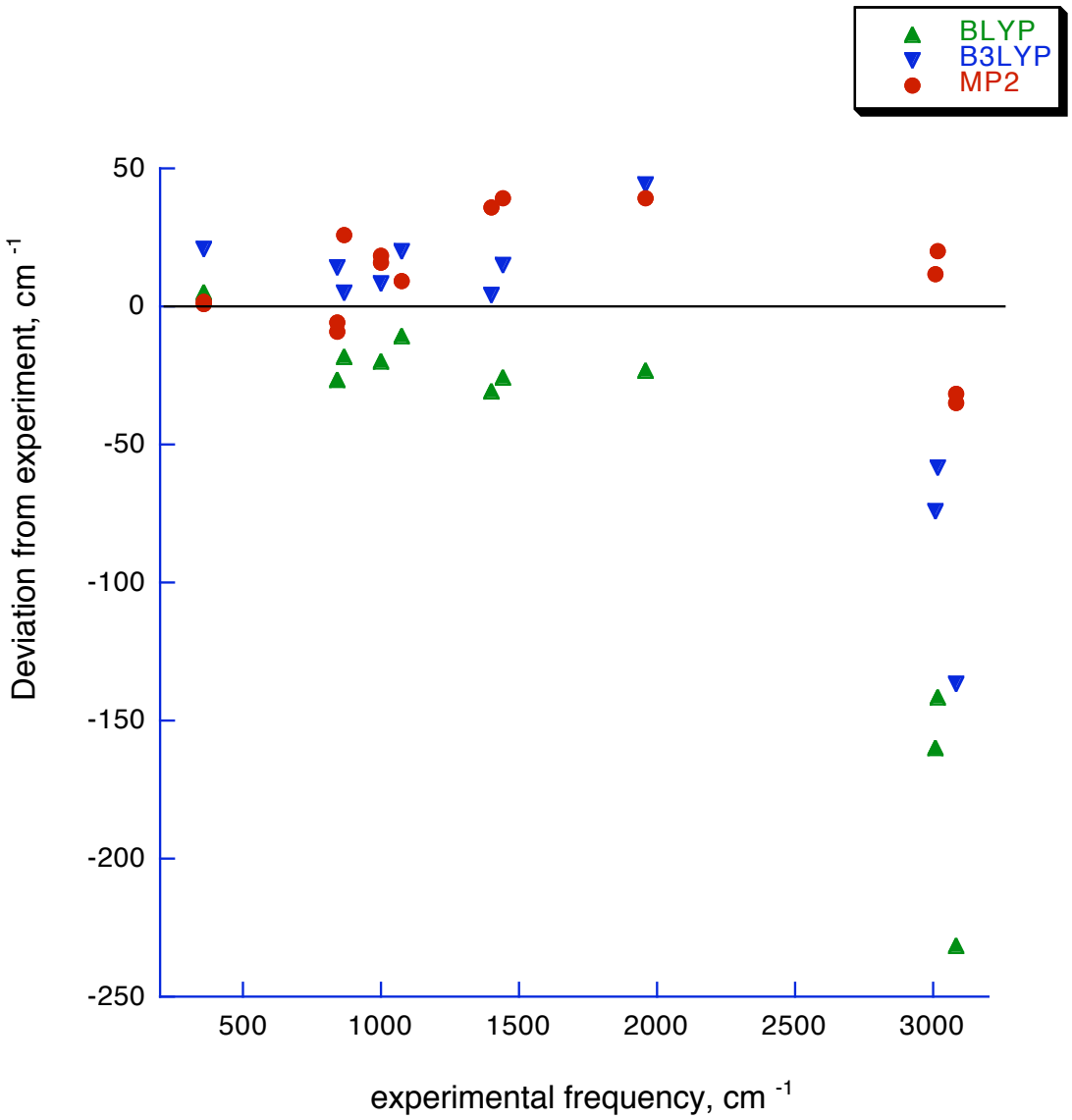

BLYP
B3LYP
MP2
50
0
-50
-100
-150
-200
-250
500
1000
1500
2000
2500
3000
Deviation from experiment, cm -1
experimental frequency, cm -1

Fig. 2

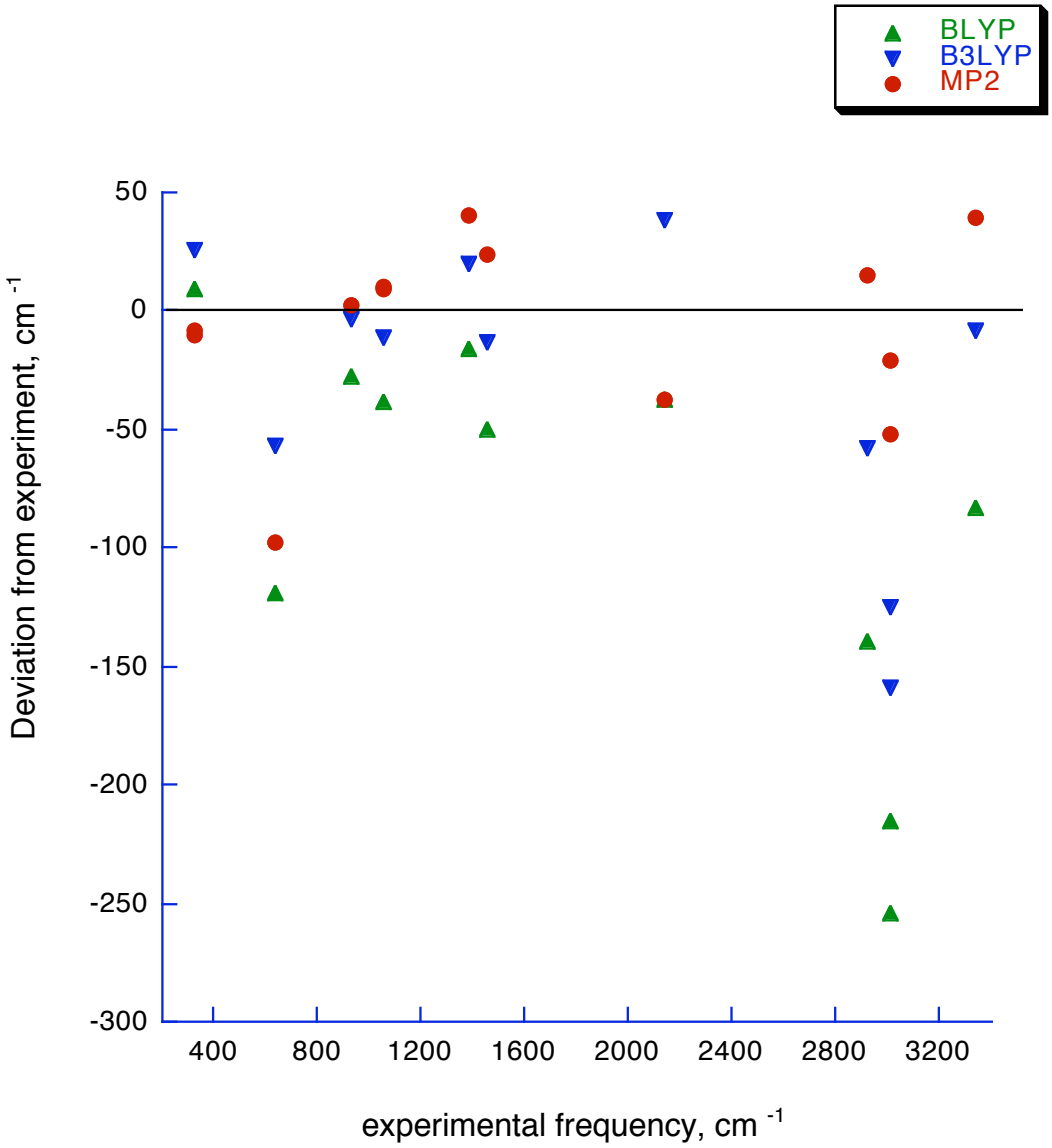

BLYP
B3LYP
MP2
50
0
-50
-100
-150
-200
-250
-300
400
800
1200
1600
2000
2400
2800
3200
Deviation from experiment, cm -1
experimental frequency, cm -1

Fig. 3

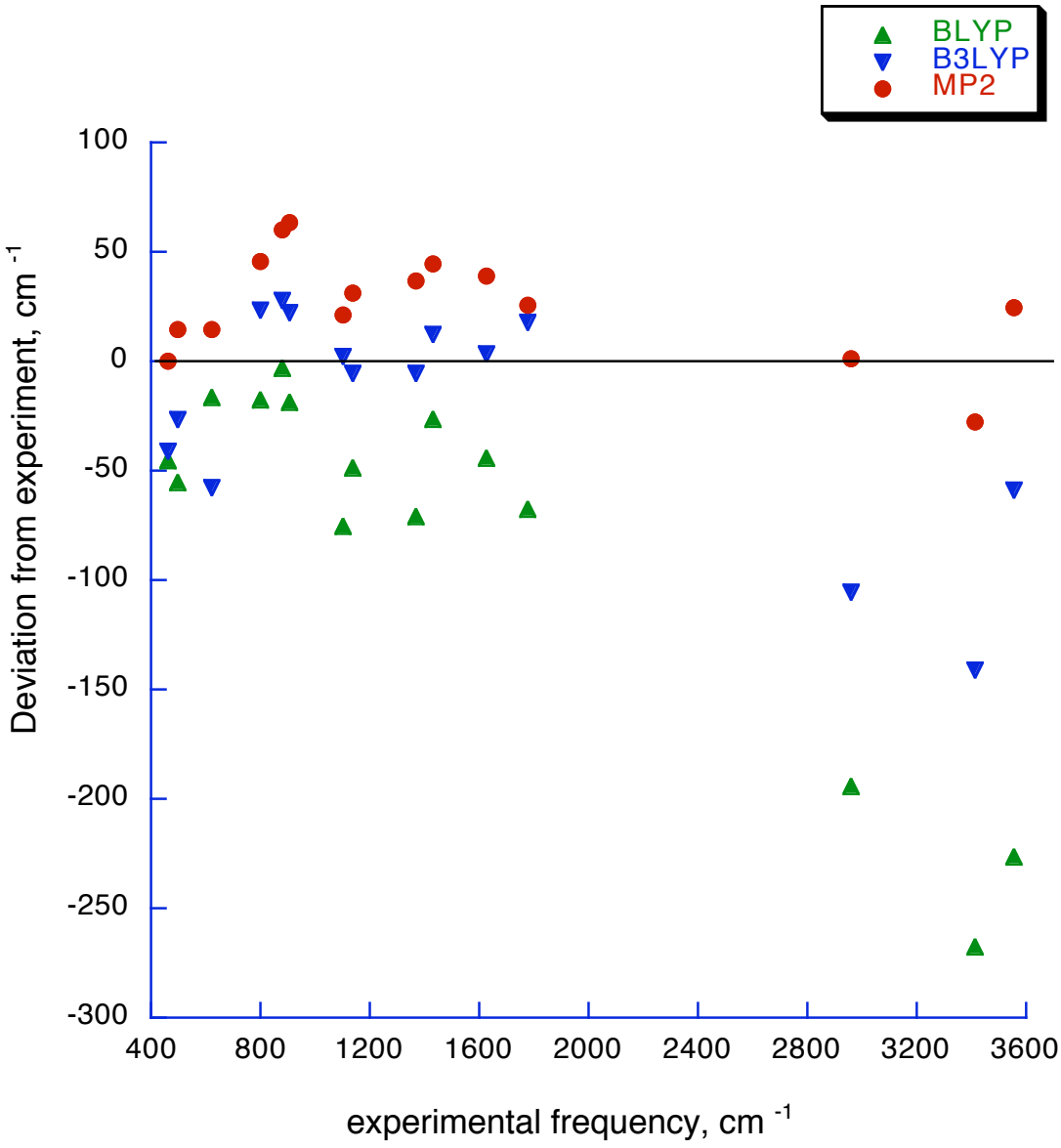

BLYP
B3LYP
MP2
100
50
0
-50
-100
-150
-200
-250
-300
400
800
1200
1600
2000
2400
2800
3200
3600
Deviation from experiment, cm -1
experimental frequency, cm -1

Fig. 4

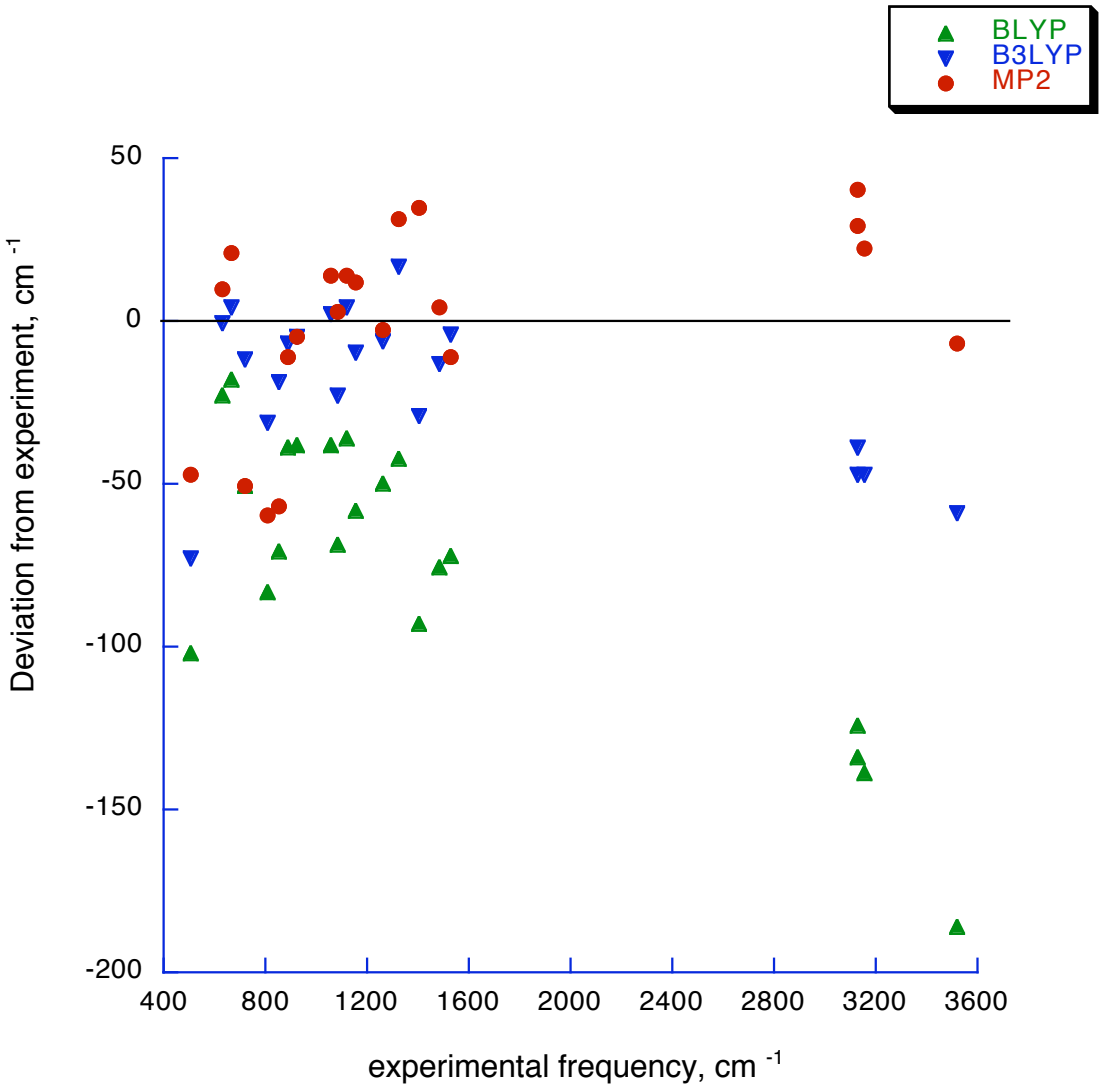

BLYP
B3LYP
MP2
50
0
-50
-100
-150
-200
400
800
1200
1600
2000
2400
2800
3200
3600
Deviation from experiment, cm -1
experimental frequency, cm -1

Fig. 5

Table 1. Vibrational frequencies for allene, cm^{-1}.

Mode	BLYP/TZP		B3LYP/TZP		MP2/TZP		exp.[a]	Description
	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf		
1	3112	2854	3196	2949	3293	3054	3086	CH_2 asym stretch
2	3112	2854	3196	2949	3293	3051	3086	CH_2 asym stretch
3	3051	2873	3128	2957	3203	3035	3015	CH_2 sym stretch
4	3047	2847	3124	2933	3202	3019	3007	CH_2 sym stretch
5	1984	1934	2049	2001	2043	1996	1957	CC stretch
6	1463	1417	1500	1458	1511	1482	1443	CH_2 bend
7	1414	1367	1444	1402	1464	1434	1398	CH_2 bend
8	1083	1062	1113	1093	1102	1082	1073	CC stretch
9	996	979	1022	1007	1027	1017	999	CH_2 rock
10	996	979	1022	1007	1027	1015	999	CH_2 rock
11	859	847	882	870	904	891	865	CH_2 twist
12	833	814	875	855	819	835	841	CH_2 wag
13	833	814	875	855	819	832	841	CH_2 wag
14	370	360	382	376	349	357	355	CCC deform
15	370	360	382	376	349	356	355	CCC deform

[a] Reference 27

Table 2. Vibrational frequencies for propyne, cm^{-1}.

Mode	BLYP/TZP		B3LYP/TZP		MP2/TZP		exp.[a]	Description
	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf		
1	3402	3251	3472	3326	3514	3373	3334	CH stretch
2	2999	2754	3083	2849	3189	2987	3008	CH_3 asym stretch
3	2999	2793	3083	2883	3189	2956	3008	CH_3 asym stretch
4	2954	2778	3029	2860	3103	2933	2918	CH_3 sym stretch
5	2156	2105	2228	2180	2160	2105	2142	CC stretch
6	1436	1402	1474	1439	1522	1476	1452	CH_2 bend
7	1436	1402	1474	1439	1522	1476	1452	CH_2 bend
8	1373	1366	1413	1402	1449	1422	1382	CH_3 umbrella
9	1012	1015	1044	1042	1076	1063	1053	CH_3 rock
10	1012	1015	1044	1042	1076	1062	1053	CH_3 rock
11	916	903	941	928	950	933	931	C-C stretch
12	599	514	653	576	594	535	633	CCH bend
13	599	514	653	576	594	535	633	CCH bend
14	309	337	334	354	292	320	328	CCC bend
15	306	337	331	354	292	318	328	CCC bend

[a] Reference 27

Table 3. Vibrational frequencies for the lowest conformer of glycine, cm^{-1}.

Mode	BLYP/DZP		B3LYP/DZP		MP2/DZP		exp.[a]	Description
	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf		
1	3607	3333	3765	3501	3829	3585	3560	OH stretch
2	3493	3142	3612	3269	3688	3382	3410	NH stretch asym
3	3399	3112	3519	3256	3590	3343		NH stretch sym
4	3038	2791	3116	2882	3213	2986		CH stretch asym
5	2975	2764	3057	2853	3148	2959	2958	CH stretch sym
6	1746	1711	1831	1797	1836	1805	1779	C=O stretch
7	1628	1586	1672	1633	1702	1669	1630	HNH bend
8	1414	1402	1457	1441	1495	1473	1429	HCH bend
9	1361	1302	1410	1368	1443	1410	1373	CO(H),CC stretch
10	1343	1291	1385	1330	1410	1377		CCN bend
11	1270	1213	1312	1266	1327	1290		NCH_2 bend
12	1160	1111	1191	1154	1205	1186		CCN oop bend
13	1111	1087	1159	1130	1195	1167	1136	CN stretch
14	1072	1026	1131	1103	1155	1122	1101	CO_2 bend
15	911	888	936	929	975	970	907	CNH_2 umbrella
16	900	880	925	911	937	943	883	$NCCO_2$ tors
17	790	783	826	824	852	847	801	C-CO_2 stretch
18	654	602	665	561	665	633	619	CO_2 oop bend
19	605	514	629	628	636	613		NCCO(H) shear
20	528	444	522	473	516	514	500	OCOH tors
21	466	417	458	422	467	463	463	NCCOH shear
22	430	370	441	402	259	270		NCCO shear
23	248	258	255	269	240	351		HNHC tors
24	126	130	114	133	58	143		NCCO(H) tors

[a] Reference 28

Table 4. Vibrational frequencies for imidazole, cm^{-1}.

Mode	BLYP/DZP		B3LYP/DZP		MP2/DZP		exp.[a]	Description
	harm	cc-vscf	harm	cc-vscf	harm	cc-vscf		
1	3555	3331	3675	3458	3740	3510	3517	NH stretch
2	3209	3021	3293	3113	3366	3182	3160	CH stretch
3	3187	3009	3267	3094	3345	3173	3133	CH stretch
4	3175	2998	3259	3085	3337	3161	3132	CH stretch
5	1483	1454	1549	1521	1553	1515	1526	CC stretch
6	1447	1406	1504	1469	1525	1486	1482	CN stretch
7	1339	1314	1405	1378	1490	1442	1407	CN stretch
8	1314	1287	1373	1346	1393	1360	1329	CN stretch
9	1242	1209	1282	1253	1283	1256	1259	CH rocking
10	1126	1101	1173	1149	1194	1171	1159	ring deformation
11	1096	1086	1134	1126	1163	1136	1122	CN stretch
12	1042	1022	1079	1062	1112	1088	1085	CH rocking
13	1020	1019	1063	1059	1088	1071	1057	CH rocking
14	893	887	925	920	932	920	925	ring deformation
15	851	853	885	885	893	881	892	ring deformation
16	796	786	847	838	787	800	857	oop CH wagging
17	749	729	801	781	762	752	812	oop CH wagging
18	683	673	721	712	681	673	724	oop ring torsion
19	653	646	675	668	667	685	664	oop CH wagging
20	614	605	636	627	642	638	628	oop ring tosion
21	487	407	512	436	541	462	509	oop NH wagging

[a] Reference 29